

## THERMAL BEHAVIOR OF SEVERAL Fe–Ni ALLOYS PREPARED BY MECHANICAL ALLOYING AND RAPID SOLIDIFICATION

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Several Fe–Ni–P–Si alloys were produced in an amorphous state by mechanical alloying and rapid solidification. Thermal behavior of the as prepared alloys was analyzed and compared with identical alloys stored during 1 and 2 years. During annealing time, several exothermic processes related to the structural relaxation were detected at low temperature and with further crystallization at high temperature. As increasing the storage time, the powdered samples were relaxed at lower temperatures. The activation energy,  $E$ , of the main crystallization process varies between 2.7 and 4.7 eV at<sup>-1</sup>. The  $E$  values obtained remains similar with the storage time.

Small contamination from the milling tools was found. Furthermore, powdered alloys are more sensible to oxidation processes than as quenched ribbons.

**Keywords:** Fe–Ni based alloys, mechanical alloying, melt spinning, thermal stability

### Introduction

Ferromagnetic iron based alloys can be produced by both rapid quenching (RQ) and mechanical alloying (MA). Fe–Ni based amorphous alloys produced by rapid solidification techniques have excellent soft magnetic properties. The magnetic properties of mechanically attrited materials are inferior [1, 2] to rapidly quenched materials and contamination from the milling tools may be a serious problem. Nevertheless, ribbons not attain a more significant level of applicability because their form limits their technological use [3, 4].

During last decades, several papers were dedicated to the thermal stability analysis of powdered alloys as well as quenched ribbons [5–7]. The use of thermal analysis on materials stability is well established [8, 9]. One of the main problems is related with the oxidation, especially of the powdered alloys [10, 11]. Furthermore, during annealing partial oxidation may be induced [12]. It is well known that oxides presence can modify drastically the thermomagnetization behavior [13]. This paper deals with the analysis of the thermal evaluation of powdered and quenched amorphous alloys and their respective time evolution, interest of the P/M industry.

### Experimental procedure

The compositions analyzed in this work were Fe<sub>40</sub>Ni<sub>40</sub>Si<sub>14</sub>P<sub>6</sub>, Fe<sub>40</sub>Ni<sub>40</sub>Si<sub>10</sub>P<sub>10</sub>, Fe<sub>40</sub>Ni<sub>40</sub>Si<sub>6</sub>P<sub>14</sub>, and Fe<sub>60</sub>Ni<sub>20</sub>Si<sub>10</sub>P<sub>10</sub>, labeled as A, B, C and D respectively.

In MA, powders (particle size up to 25 μm) of elemental Fe, Ni, P and Si were loaded into hardened steel vial together with steel balls inside an argon filled glove box. The ball millings were performed in a planetary type mill (Frisch Pulverisette 7). The ball-to-powder mass ratio was 5:1 and the milling intensity was held at an intensity setting of 7. The final milling time for amorphous materials was 32 h. The amorphous melt-spun alloys A, B and C were produced, in ribbon form, by quenching the molten alloy on the surface of a rapidly spinning (~35 m s<sup>-1</sup>) copper wheel under Ar atmosphere. In this case, the Fe<sub>3</sub>P compound was used to prevent P sublimation. The thickness and width of the resulting ribbons were about 30 μm and 2.5 mm, respectively. The alloys were deposited in a glove-box during two years.

The thermal stability of the metastable phases formed was tested, by studying their behavior on heating, in a differential scanning calorimeter (Mettler Toledo DSC30), under a pure Ar atmosphere. The thermal characterization was complemented by thermogravimetry (TG) under an argon atmosphere in a TGA851 Mettler Toledo equipment. The contamination was analyzed by induction coupled plasma (ICP) in a Liberty ICP–Varian equipment, by flame absorbance atomic spectroscopy (FAAS) in a Varian AA-1275 device and with the energy dispersive X-ray microanalysis (EDX) system coupled to a SEIZZ DSM960 A scanning electron microscope.

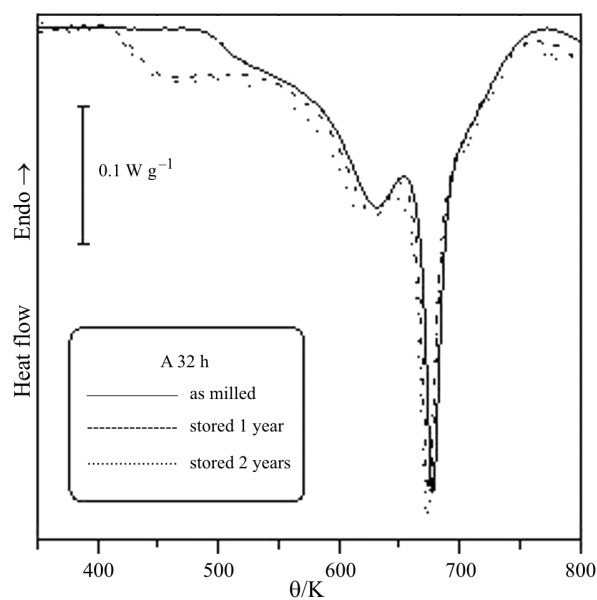
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## Results and discussion

In the MA alloys, a serious problem is the potential for significant contamination from the milling media (balls and vial). Furthermore, oxygen presence due to the oxidation produced by contact with air atmosphere during preparation of powders for analysis was usually detected. This contamination is favored by the high surface/volume ratio of the small particles. The contamination measured by combined data obtained from EDX, FAAS and ICP in the powdered alloy increases with the milling time. Nevertheless, the results show only slight (<2.5 at.%) contamination from the milling tools (Fe, Ni and Cr) after 32 h. The values are similar in all alloys. Several analysis were performed and the oxygen presence detected was:  $1.5 \pm 0.6$ ,  $1.4 \pm 0.5$ ,  $1.6 \pm 0.5$  and  $2.8 \pm 0.5$  at.% for alloys A, B, C and D respectively. Alloy D has the higher Fe content. Furthermore, as increasing the storage time, the Fe content diminishes  $\sim 2\text{--}4$  at.%, probably due to the formation of a superficial layer of iron oxides that is easily eliminated of the powdered material. No significant oxidation was detected in as quenched alloys (<0.5 at.%). Similar results were found in Fe based alloys with similar composition [14].

Thermal study was performed by DSC. Stability, an important factor on amorphous metallic structures is related to the relaxation phenomena and crystallization, which is usually a thermally activated process of transition from a disordered amorphous structure to an ordered crystal structure.

As shown in Fig. 1, in the DSC analysis of the MA alloy A, there is a broad hump in the temperature ranges of 450–500 K, associated with relief of internal stresses.

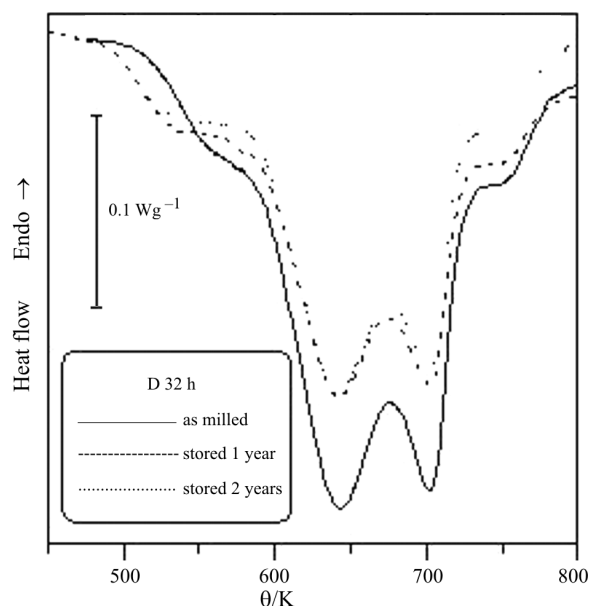


**Fig. 1** DSC scans of alloy A milled during 32 h: as milled, stored one year and stored two years

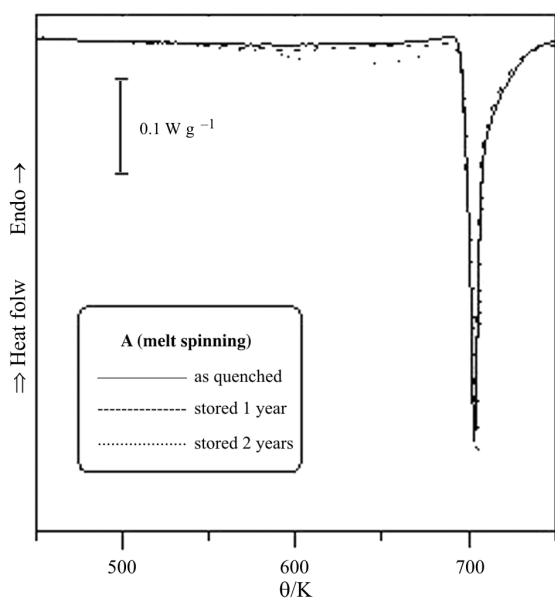
The exothermic peaks over 600 K correspond to the crystallization processes. The two overlapped crystallization peaks were also found in previous analysis of similar alloys and are related to the presence of Ni [15]. Similar behavior was found in alloy D, Fig. 2, where the two peaks associated to different Fe and Ni environments have similar intensity. As increasing the storage time, the powdered samples were relaxed at lower temperatures. This effect was determined from the starting temperature of the broad process and is more clear (>50°C) in alloy A. Notwithstanding the long storage times, the same samples were used. Nevertheless, the effect could not be exclusively time storage dependent. The total area associated to the thermal process was measured by integration using a base line. The value diminishes about 30% in alloy D milled for 32 h.

Nevertheless, only one main crystallization peak was found in RQ alloys. Furthermore, in Fig. 3, the structural relaxation phenomenon detected in the mechanically tensioned powders is not so important in as-quenched ribbons [16], but appears more clearly as increasing the storage time. The crystallization process of the as-quenched ribbons began at higher temperature. Therefore, the metastable phases obtained by rapid solidification are more thermally stable than analogous phases in mechanically alloyed powders [16, 17]. Similar behavior was found in nanocrystalline mechanically alloyed Fe–Zr–B–(Cu) alloys [18, 19].

The apparent activation energy,  $E$ , for the main crystallization process of alloys milled or quenched can be evaluated using the Kissinger equation:  $\ln(\beta/T_p^2)$  vs.  $1/T_p$  with  $\beta$  the heating rate and  $T_p$  the peak temperature [20]. The crystallization data have been collected from DSC curves, obtained with different heating



**Fig. 2** DSC scans of alloy D milled during 32 h: as milled, stored one year and stored two years



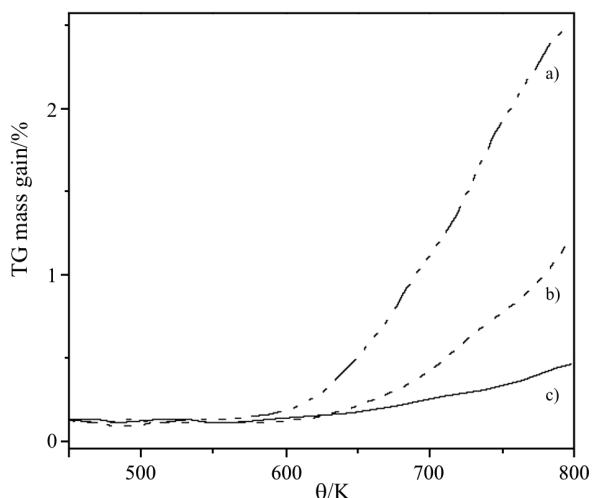
**Fig. 3** DSC scans of alloy A obtained by melt spinning: as quenched, stored one year and stored two years

rates (2.5, 5, 10, 20 and 40 K min<sup>-1</sup>). The activation energy,  $E$ , of the main crystallization process remains similar with the storage time. Nevertheless, sometimes the beginnings of the crystallization processes are slightly shifted (<10°C). The  $E$  values are given in Table 1.

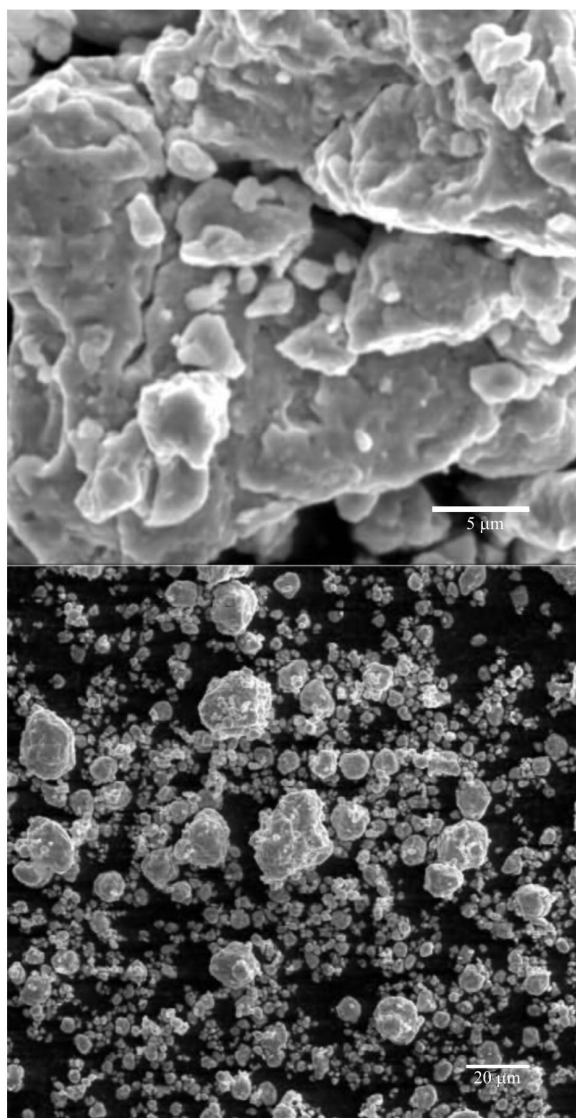
The TG analysis shows that heating of powdered materials induces a significant mass increase associated to thermally activated oxidation. Similar behavior was found in the TG analysis of nanocrystalline Fe–Ni solid solutions prepared by mechanical alloying [21]. Figure 4 shows the TG curve of ribbon A (a), MA alloy A (b) and MA alloy D (c). Lower thermally induced mass increase was found in ribbons where the surface/volume ratio is lower. Furthermore, in the amorphous powdered alloys, increasing Fe content favors this process. Recently, special attention has been paid to nanocrystalline alloys obtained by controlled crystallization of the amorphous alloys. It was found in FeNbB alloys that the amorphous alloys show a significant oxidation resistance over those of the nanocrystalline alloys with the same composition [22].

**Table 1** Activation energy,  $E$ , of the main crystallization process: time storage evolution

Sample	$E/ \text{eV at.}^{-1}$		
	As prepared	Stored 1 year	Stored 2 years
A 32 h MA	3.8	3.6	3.8
D 32 h MA	2.9	2.7	2.8
A (melt spinning)	4.7	4.6	4.6



**Fig. 4** TG scans: a – ribbon A as quenched, b – powdered alloy A as milled and c – powdered alloy D as milled



**Fig. 5** SEM micrographs of alloy D milled for 32 h

Furthermore, the morphology of the powders was analyzed by scanning electron microscopy. As an example, Fig. 5 shows two micrographs that correspond to alloy D. No significant changes were found with storage time.

## Conclusions

Several Fe–Ni based amorphous alloys were produced by mechanical alloying and rapid solidification. The contamination in the powdered alloy increases with the milling time. Nevertheless, the results show only slight (< 2.5 at.%) contamination from the milling tools (Fe, Ni and Cr). The oxygen presence detected was:  $1.5 \pm 0.6$ ,  $1.4 \pm 0.5$ ,  $1.6 \pm 0.5$  and  $2.8 \pm 0.5$  at.% for alloys A, B, C and D respectively. Alloy D has the highest Fe content. The Fe content diminishes as increasing the storage time, between 2 and 4 at.%, probably due to the formation of a superficial layer of iron oxides which is easily eliminated from the powdered material.

The powdered samples were relaxed at lower temperatures as increasing the storage time. The total area associated to the thermal process diminishes about 30% in alloy D. The structural relaxation phenomenon is not so important in as-quenched ribbons, but appears more clearly as increasing the storage time. The amorphous phases obtained by rapid solidification are more thermally stable than analogous phases in mechanically alloyed powders.

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